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(11) Publication number:

0 426 949 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90113118.5

(51) Int. Cl.⁵: C01B 15/037

(22) Date of filing: 10.07.90

A request for correction on page 15 of the description has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 2.2).

(30) Priority: 09.11.89 **GB 8925376**

(43) Date of publication of application:
15.05.91 Bulletin 91/20

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI NL SE

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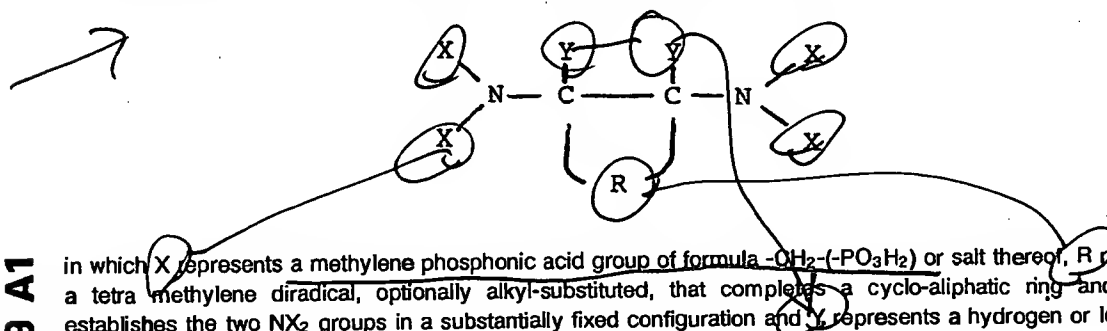
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(54) Stabilisation of concentrated hydrogen peroxide solutions.

(57) Concentrated solutions of hydrogen peroxide tend to decompose on storage, thereby losing their effectiveness, amongst other reasons by virtue of interaction with contaminating transition metals.

Peroxygen compounds are stabilised by contact with a stabilising amount of compound of general formula:-



in which X represents a methylene phosphonic acid group of formula $-CH_2-(-PO_3H_2)$ or salt thereof, R represents a tetra methylene diradical, optionally alkyl-substituted, that completes a cyclo-aliphatic ring and thereby establishes the two NX_2 groups in a substantially fixed configuration and Y represents a hydrogen or lower alkyl group.

Preferably, the solutions contain additionally one or more co-stabilisers, including stannate, phosphates, hydroxybenzoic acid, citric acid and nitrate.

The stabiliser system can enable the solution to be diluted, even with municipal water.

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STABILISING CONCENTRATED HYDROGEN PEROXIDE SOLUTIONS

The present invention relates to a process for stabilising concentrated solutions of hydrogen peroxide and in particular a process in which an ion-chelating stabiliser is incorporated therein.

Concentrated aqueous solutions of hydrogen peroxide suffer from the problem of decomposition during storage or use and there have been many suggestions given as to possible causes of the decomposition. These include the application of excess heat, exposure to various types of radiation and contact with various sorts of container surface, but one of the most widespread causes is contamination of the peroxidic solution with certain catalysts, often in solution or as solid particles in contact therewith. Such catalysts often are transition metals, of which the most prevalent are the first row metals such as iron, copper, vanadium, cobalt, chromium and nickel.

There have been many proposals for stabilising hydrogen peroxide solutions, by which herein is meant reducing the rate of decomposition of the peroxide. Hydrogen peroxide is normally transported and stored in the form of concentrated solutions so as to minimise the cost of transporting and storing more water than is necessary. The high concentration of the hydrogen peroxide, a widely used oxidant, and the likelihood that the solution may be stored for some considerable time before it is used imposes a particular set of requirements upon a process for stabilisation. In particular, the stabiliser is desirably effective under acidic conditions and is resistant to in situ oxidation, thereby retaining its effectiveness during prolonged storage. Secondly, since it is often desirable to employ the peroxide at a lower concentration than that at which it is transported, the dilutability of the solution is often of some importance.

Traditionally, concentrated solutions have been formed by distilling more dilute solutions, and stabilised by the incorporation of small amounts of inorganic stabilisers and particularly pyrophosphate and/or silicates. In more recent times, the use has been suggested of organic chelating compounds, including especially certain classes of organic carboxylic acids and organic phosphonic acids. Such chelates have been successful up to a point at stabilising a range of hydrogen peroxide solutions, including concentrated solutions, but the objective always remains to produce even more effective stabilising systems.

For many purposes, two of the most highly favoured chelating stabilisers gaining in popularity in recent years have been 1,1,1-hydroxyethylenediphosphonic acid (abbreviated herein to HEDP) and ethylene diamine tetramethylenephosphonic acid or its sodium or potassium salt thereof, abbreviated herein to EDTMP. Two other related stabilisers that have also been commercially employed likewise are nitrilotrimethylenephosphonic acid/salts (NTMP) and diethylene triamine pentamethylenephosphonic acid/salts (DTPMP). The use of these stabilisers as the sole stabiliser or in conjunction with other compounds has been described in a large number of published patents including USP 3122417 (Henkel), USP 3234140 (Monsanto), USP 3383174 (FMC), USP 3387939 (Du Pont), USP 3542918 (Therachemie Chemisch Therapeutische), USP 3701825 (FMC), USP 3740187 (Monsanto), USP 3860391 (Benckiser-Knapsack), USP 3865435 (Kennecott Copper), USP 3903244 (FMC), USP 4059678 (FMC), USP 4070442 (Du Pont), USP 4239643 (Monsanto), USP 4210565 (Oxysynthese), USP 4304762 (Unilever), and USP 4347149, 4497725 and 4525291 (all to Interlox Chemicals).

It is an objective of the instant invention to provide a stabiliser for concentrated hydrogen peroxide solutions which a more effective stabiliser under at least some conditions than the organic phosphonic acid stabilisers that have been identified hereinbefore.

The incorporation of a wide range of phosphonic acid compounds in dilute alkaline solutions of hydrogen peroxide used for bleaching cellulosic fibrous material has been suggested in a number of the foregoing specifications and in some considerable detail by Ciba-Geigy AG in EP-A-0 210 952, including a number of compounds in which aminomethylene phosphonic acid groups were dependent from a carbocyclic nucleus. However, none of the substituted carbocyclic compounds were employed in the Examples, so that the specification provides no basis for asserting that any of those compounds would have superior stabiliser properties to the compounds that were exemplified, let alone a teaching to select a non-exemplified compound for improving the stability and/or dilutability of acidic concentrated hydrogen peroxide solutions.

According to one aspect of the present invention there is provided a process for stabilising a concentrated aqueous hydrogen peroxide solution against decomposition in which the peroxide compound is brought into contact with an effective amount of a stabiliser characterised in that the stabiliser has the general formula:-

In the context of the instant invention, the range of concentrated hydrogen peroxide solutions includes the grades of concentrated hydrogen peroxide that are typically sold and transported in many parts of the world, and fall within the limits of approximately 25% w/w to 85% w/w, and including specifically grades of about 100 volum , 35% w/w, 50% w/w, 65-70% w/w and 80-85% w/w. The pH of the concentrated solution normally lies in the range of from pH 0 to pH 6, and in many instances is from about pH 2 to 4.

The stabilised solution can be used for a very wide variety of different types of uses, after any necessary dilution and or pH adjustment. Such uses include those in strongly acidic metal-treatment solutions, acidic or alkaline solutions for metal extraction, separation or purification, use in disinfection and in alkaline solution for a range of different bleaching processes, including bleaching cotton or other textile fabrics, paper, pulp, straw, waste plant material, and domestically in household bleaching/washing operations or for keratinous material. Solutions containing the invention stabiliser are particularly suitable for use in chemical synthesis and can be used in conjunction with the known metal catalysts, for example iron to form Fenton's reagent, with continued reactivity despite the fact that such metals will be complexed by the stabiliser.

The concentration of stabiliser to employ in order for it to be effective is usually very low in comparison with the weight of peroxygen compound, but the actual amount will often take into account such factors as the extent to which the composition is already or likely in the future to be contaminated, especially with catalysts known to be able to decompose peroxygen compounds, the pH of the solution and the extent of stabilisation needed in use. In many instances, and especially in acidic conditions, the weight ratio of the peroxygen compound to stabiliser will be selected in the range of from 140:1 to 70000:1. It is often expressed alternatively in terms of simply the amount of stabiliser in the peroxygen composition, and this normally is at least 10ppm w/w, and generally is not more than 5000ppm, irrespective of the peroxygen compound concentration. The actual amount typically employed varies between different purposes for the composition. Thus, for example, electronic grade solutions which tend to employ the purest ingredients normally contain 10 to 50 ppm of the stabiliser, grades of solution intended for chemical syntheses, such as epoxidations and controlled organic oxidations often contain from 50 to 1000 ppm of the stabiliser, solutions intended for treating contact lenses typically contain the stabiliser in the region of 1000ppm and solutions intended for the treatment of metals, such as metal pickling or polishing solutions often contain high concentrations of stabiliser of 1000 to 5000 ppm to counteract high concentrations of transition metal catalysts which such solutions eventually contain. It will be understood that the invention stabilisers can be substituted for previously available phosphonic acid stabilisers such as HEDP or EDTMP in substantially the same amounts as have been described for the use of those prior stabilisers.

Although the invention stabiliser can be employed, if desired, as the sole stabiliser, it can also be employed advantageously in combination with the classes of other materials that have been described hitherto as stabilisers for hydrogen peroxide. Advantageously, under certain conditions, and typically expressed in general terms when the phosphonate stabiliser represents the major weight fraction, synergism between the stabilisers is apparent. One such class of co-stabilisers comprises organic acids containing two or more functional groups. These groups can be carboxylic acid groups or alternatively one or more of them can be an hydroxyl, or amino group. Examples of that type of co-stabiliser include citric acid and related acids like gluconic acid, and aromatic compounds like salicylic acid, p-hydroxybenzoic acid, and anthranilic acid.

A further class of co-stabiliser comprises phosphates, by which term is meant not only phosphoric acid itself and salts thereof, but also the various condensed phosphate species including especially tetrapyrophosphates and hexametaphosphates.

The aforementioned co-stabilisers often demonstrate synergy when employed in an amount of up to about 1 part per part by weight of the invention stabilisers, such as in the range of 1:10 to 1:1 parts co-stabiliser.

Additionally, the invention stabilisers can be employed with other well-known conventional stabilisers such as soluble silicates, and in particular magnesium silicates, stannates and particularly sodium stannate and the heretofore commercialised phosphonate stabilisers like HEDP, EDTMP, NTMP, DTPMP and the corresponding amino-carboxylic acid stabilisers like EDTA and DTPA. The amounts of such additional stabilisers can be used at the discretion of the formulator, but often are individually selected in the range of 0.1 to 10 parts w/w of the invention phosphonate stabiliser.

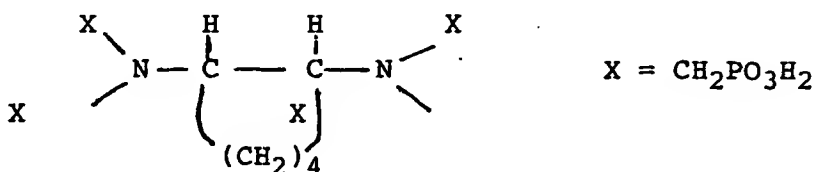
Advantageously, it has been found that a particularly effective combination of stabilisers that is well suited to dilution with municipal water supplies comprises the CDTMP plus sodium stannate, preferably selected in concentrations of respectively 10 to 500 mg/l and 0.5 to 10 mg/l (calculated as Sn). Additionally, the invention stabiliser solution can also include an agent such as nitric acid or soluble salt thereof which can passivate certain metal surfaces such as aluminium which has been a favoured material in which to

storing aqueous hydrogen peroxide solutions. Typically, nitrate can be employed in a weight ratio of up to twice the weight of the invention stabiliser whilst retaining or even augmenting the stability of hydrogen peroxide.

Having described the invention in general terms, specific embodiments will be given hereinafter in greater detail by way of example only.

Example 1 and Comparison C2.

In this Example the effectiveness at stabilisation is demonstrated by introduction of an aminocompound, CDTMP having the formula:-



compared with HEDP in the comparison.

The test is carried out by dilution of unstabilised distilled 85% w/w hydrogen peroxide to 70% w/w with deionised water, introducing into the aqueous acidic solution the respective stabiliser compound to a concentration of 1000mg/kg and further diluting the solution to 35% w/w concentration. Duplicate samples, each of 25mls of the 35% w/w solution were then doped with a mixture of transition metal compounds known to be able to catalyse decomposition of the hydrogen peroxide, namely iron to a concentration of 3.45×10^{-3} g Fe³⁺/litre and copper to a concentration of 7.85×10^{-4} g Cu²⁺/litre. The samples were then held for 3 hours at 40°C and the volume of gas generated was measured by a water displacement method at ambient pressure (plus the very small extra pressure resulting from the few centimetres head of displaced water.) It was found that under the conditions of this test, the mean rate of gassing in Example 1 was only 6.0×10^{-3} ml/min compared with a mean gassing rate from the comparison HEDP of 23.2×10^{-3} mls/min under the same test conditions. This shows that the invention stabiliser was markedly more effective than HEDP. When the same weight of EDTMP (ethylene diamine tetramethylene phosphonate), a comparison stabiliser, was substituted for CDTMP in this test, its mean gassing rate was 8.0×10^{-3} ml/min which is significantly worse than the results for CDTMP.

Example 3 and comparison 4

In this Example, the effectiveness at peroxidic stabilisation by introduction of CDTMP is demonstrated under the following conditions which simulate the effect of on-site dilution of concentrated hydrogen peroxide that has been transported and which typically uses a local water supply that contains metal contaminants.

A solution of 70% w/w hydrogen peroxide solution containing 1000mg/litre of the stabiliser was prepared in the same way as for Example 1, and was then stored at ambient temperature that was about 20 to 25°C during the day. Periodically, three samples, each of 25mls, were prepared by diluting extracts to 35% w/w concentration with deionised water and introducing a mixture of decomposition catalysts to concentrations of respectively:-

- 1.2×10^{-4} g/litre Al³⁺
- 1.2×10^{-4} g/litre Fe³⁺
- 2.4×10^{-5} g/litre Cu²⁺
- 1.2×10^{-5} g/litre Mn²⁺
- 6.0×10^{-6} g/litre Cr⁶⁺

The samples were then heated to 100°C for three hours in glass reaction tubes and the amount of gas evolved was measured. The effectiveness of the stabiliser for long term storage was determined by observing what change there was in the extent of gas evolution after increasing periods of storage of the 70% w/w solution.

The mean rate of gas evolution from the 25ml samples was 0.033 ml/min on the day when the stabiliser

was introduced into the 70% w/w solution, and after respectively 2 months, 4 months and 5 months storage, the mean rates were 0.034, 0.039, and 0.049 ml/min.

By way of comparison, in comparison C4, exactly the same test was carried out using the same weight of HEDP instead of CDTMP and the mean gassing rates were respectively 0.021 ml/min on the day when the 70% w/w solution was produced, and 0.047 ml/min after 2 months storage.

From the figures for Example 3, it can be seen that CDTMP is not only a very good stabiliser upon introduction into a peroxygen composition, but also that it retains its stabilising properties very well during storage for extended periods. It can consequently be deduced that even if CDTMP is in some way interacting in solution with the other components, the resultant product also demonstrates stabilising properties.

By comparing the results obtained for Example 3 with those for comparison 4, it will be observed that the invention stabiliser was more effective expressed on a weight/weight basis for long term storage, and more so if expressed on the basis of stabilisation conferred per unit weight of phosphonic acid group, since the proportion of phosphonic acid in HEDP is greater than in CDTMP.

Example 5

In this Example, diluted solutions of hydrogen peroxide (3 % w/w), approx, in biologically pure water, i.e. suitable for use in sterilising contact lenses, were stabilised by introduction of CDTMP at a concentration of from 50 to 1000 ppm. Some of the CDTMP products had been rendered acid with sulphuric acid and some with hydrochloric acid. The samples of solution were stored at ambient temperature in small stoppered polyethylene bottles that would permit the gas pressure to equalise with the external atmospheric pressure. The solutions were periodically tested for residual available oxygen by the standard test using potassium iodide and potassium permanganate. After 9 weeks, within the limits of error of the testing procedure, there was no apparent loss of active oxygen from any of the samples, and indeed on average they showed an apparent gain of about 1% available oxygen, a finding that is consistent with minimal water loss by evaporation on storage. This test shows not only how effective CDTMP is as a stabiliser, but also that the stabiliser is somewhat tolerant to the presence of chloride ions, which have been implicated in peroxidic decomposition in some conditions.

Example 6

In this Example, CDTMP stabiliser was introduced into 35% w/w aqueous hydrogen peroxide solutions at a concentration of from 20 to 1000 ppm. Intermediate concentrations were 50, 100, 200 and 500 ppm. The solutions were stored at 32°C in the polyethylene bottles, at a pH of approximately 3, and periodically tested for residual available oxygen content by the standard KI/KMnO₄ method. After 7 weeks storage, the solutions had fallen by about 0.1% available oxygen in 35%, i.e. 0.3%, except for the sample containing the least amount of CDTMP 20 ppm, which showed no apparent loss of available oxygen concentration. This example demonstrates that even very low concentrations of stabiliser, 6 parts per 100,000 parts w/w of hydrogen peroxide was effective at stabilisation at this pH.

Example 7

In this Example, the procedure of Example 3 was repeated, but substituting the same weight of CDTMP that had been made in the presence of sulphuric acid and was thus essentially chloride-free in place of CDTMP that contained residual low level of chloride. It was found that the gassing rate was only 0.021 ml/min for the 25 ml sample, measured on the day that the stabiliser was introduced into the concentrated hydrogen peroxide solution. This indicates that this product was even more effective as a stabiliser than the chloride-containing product.

Example 8

In this Example, the procedure of Example 1 was followed, but employing instead of 1000ppm of stabiliser respectively 500ppm of CDTMP in 8a, 500ppm of CDTMP plus 100ppm of citric acid in 8b, and

300ppm of CDTMP plus 300ppm of citric acid in 8c. It was found that relative to 8a, the rate of gassing in 8b was reduced by a factor of 1.3 and that in 8c was reduced by a factor of 2.2. This demonstrates clearly that citric acid in such proportions was cooperating, probably synergistically, with CDTMP.

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Example 9

In this Example, the procedure of Example 1 was followed, but employing instead of 1000ppm of stabiliser respectively 500ppm of CDTMP in 9a, 500ppm of CDTMP plus 100ppm of p-hydroxybenzoic acid (PHBA) in 9b, and 400ppm of CDTMP plus 200ppm of PHBA in 9c. It was found that relative to 9a, the rate of gassing in 9b was reduced by a factor of 2.0 and that in 9c was reduced by a factor of 1.3. This demonstrates clearly that p-hydroxybenzoic acid in such proportions was cooperating, probably synergistically, with CDTMP.

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Example 10

In this Example, the procedure of Example 1 was followed, but employing instead of 1000ppm of stabiliser respectively 500ppm of CDTMP in 10a, 500ppm of CDTMP plus 100ppm of sodium pyrophosphate in 10b, and 300ppm of CDTMP plus 300ppm of sodium pyrophosphate in 10c. It was found that relative to 10a, the rate of gassing in 10b was reduced by a factor of 1.6 and that in 10c was reduced by a factor of 1.3. This demonstrates clearly that sodium pyrophosphate in such proportions was cooperating, probably synergistically, with CDTMP.

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Example 11

In this Example, the procedure of Example 1 was followed, but employing instead of 1000ppm of stabiliser respectively 500ppm of CDTMP in 11a, 500ppm of CDTMP plus 100ppm of phosphoric acid in 11b, and 300ppm of CDTMP plus 300ppm of phosphoric acid in 11c. It was found that relative to 11a, the rate of gassing in 11b was reduced by a factor of 2.7 and that in 11c was reduced by a factor of 1.8. This demonstrates clearly that phosphoric acid in such proportions was cooperating, probably synergistically, with CDTMP.

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Example 12

In this Example, the procedure of Example 1 was followed, but employing instead of 1000ppm of stabiliser respectively 500ppm of CDTMP in 12a, 500ppm of CDTMP plus 100ppm of sodium nitrate in 12b, and 300ppm of CDTMP plus 300ppm of sodium nitrate in 12c. It was found that relative to 12a, the rate of gassing in 12b was reduced by a factor of 1.6 and that in 12c was reduced by a factor of 1.3. This demonstrates clearly that nitric acid though not a stabiliser in its own right in such proportions was cooperating, probably synergistically, with CDTMP.

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Example 13

In this Example, the effectiveness of the invention stabiliser systems at reducing peroxide decomposition on its dilution with municipal water is demonstrated. In each trial, aqueous hydrogen peroxide, 35% w/w, and containing the amounts of stabilisers specified, is diluted to a concentration of 6% with the municipal water supply of Luton, England and its pH is adjusted to pH2.5. The stability of the resultant solution was determined by heating 25ml samples (in triplicate) to 100°C and measuring the volume of gas evolved by decomposition of the peroxide. The average cumulative amount after 3 hours of the three samples is given below. Trial 13a which was not according to the invention is given for comparison only. In the Table, the weight of CDTMP given is that of the active ingredient, introduced in the form of a 30% w/w aqueous solution, the weight of sodium pyrophosphate is calculated as PO_4 and the weight of sodium stannate is calculated as Sn.

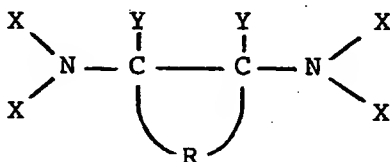
Table

No	Trial Stabiliser System - mg/l of			Gas evolved
	CDTMP	phosphate	stannate	mls
13a	-	?	60	4.7
13b	900	?	-	1.2
13c	228	?	-	2.7
13d	30	?	5	1.4

From the Table, it can be seen that it is possible to produce a dilution grade of hydrogen peroxide that omits or substantially reduces the concentration of stannate, whilst maintaining or improving the stability of the product after dilution. It can also be seen by comparing trials 13b, 13c and 13d that the addition of only 5 mg/l stannate enables a similar extent of stabilisation to be attained using only a thirtieth of the amount of CDTMP in trial 13b, thereby demonstrating synergistic cooperation between the components of the stabiliser system in 13d.

Claims

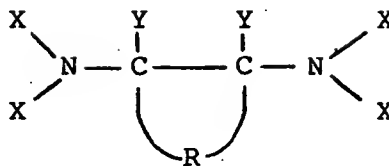
1. A process for stabilising a concentrated aqueous hydrogen peroxide solution against decomposition in which the peroxygen compound is brought into contact with an effective amount of a stabiliser characterised in that the stabiliser has the general formula:-



in which X represents a methylene phosphonic acid group of formula $-\text{CH}_2-(\text{PO}_3\text{H}_2)$ or salt thereof, R represents a tetra methylene diradical, optionally alkyl-substituted, that completes a cyclo-aliphatic ring and thereby establishes the two NX_2 groups in a substantially fixed configuration and Y represents a hydrogen or lower alkyl group.

2. A process according to claim 1 characterised in that the stabiliser is cyclohexane-1,2-diaminotetramethylene phosphonic acid.
3. A process according to claim 1 or 2 characterised in that the stabiliser is introduced into aqueous acidic solution containing hydrogen peroxide in a weight ratio of stabiliser to percompound of from 1:140 to 1:70000.
4. A process according to any preceding claim characterised in that the stabiliser is employed in conjunction with a co-stabiliser selected from organic acids containing a plurality of functional groups which can be carboxylic and/or sulphonic acid groups or hydroxyl or amino groups.
5. A process according to claim 4 characterised in that the co-stabiliser comprises an aliphatic or aromatic hydroxycarboxylic acid.
6. A process according to claim 5 characterised in that the co-stabiliser is citric acid or p-hydroxybenzoic acid.
7. A process according to any preceding claim characterised in that the stabiliser is employed in conjunction with a co-stabiliser selected from phosphates.
8. A process according to any of claims 4 to 7 characterised in that the co-stabiliser is employed in a weight ratio to the stabiliser of up to about 1:1.
9. A process according to any preceding claim characterised in that the stabiliser is employed in conjunction either or both of nitrate, and stannate.
10. A concentrated aqueous acidic solution of hydrogen peroxide stabilised by introduction of an effective

amount of a compound of formula:-



in which X represents a methylene phosphonic acid group of formula $-\text{CH}_2-(\text{PO}_3\text{H}_2)$ or salt thereof, R represents a tetra methylene diradical, optionally alkyl-substituted, that completes a cyclo-aliphatic ring and thereby establishes the two NX_2 groups in a substantially fixed configuration and Y represents a hydrogen or lower alkyl group.

11. A composition according to claim 10 and further characterised by the feature described in any one of claims 2 to 9 hereinbefore.

12. A process for stabilisation or a stabilised peroxygen composition employing a stabiliser substantially in accordance with claim 1 and any novel feature or novel combination of features described herein.



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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 3118

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	FR-A-2 643 093 (MANUFACTURE DE PRODUITS CHIMIQUES PROTEX) * page 1, paragraph 1,3; claim 2 *	1,10	C 01 B 15/037
D,X	EP-A-0 210 952 (CIBA-GEIGY) * page 1, paragraph 1 ** page 2, line 28 - page 3, line 6 @ page 3, line 25 - page 4, line 5 @ page 5, lines 1 - 3 @ page 5, paragraph 3,4 ** page 7, line 13 - page 8, line 3 *	1,4,10-12	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 01 B C 11 D
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		31 January 91	VAN BELLINGEN I.C.A.
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